Sonoma Technology, Inc.

1360 Redwood Way, Suite C
Petaluma, CA 94954-1169
707/665-9900
FAX 707/665-9800
www.sonomatech.com

California Regional PM_{10} and $PM_{2.5}$ Air Quality Study (CRPAQS)
Data Analysis Task 1.1b

EXAMINATION OF REACTIVE NITROGEN PARTITIONING AT THE BAKERSFIELD AND ANGIOLA FIELD SITES

TECHNICAL MEMORANDUM
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By:
Martin P. Buhr
Erin Shields
Elizabeth M. Simon
Stephen B. Reid
Sonoma Technology, Inc.
1360 Redwood Way, Suite C
Petaluma, CA 94954

Prepared for:
California Air Resources Board
1001 I Street
Sacramento, CA 95814

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1. INTRODUCTION

Previous studies have indicated that, under many conditions, formation of aerosol nitrate in the San Joaquin Valley (SJV) depends on the availability of nitric acid. In turn, the formation of nitric acid depends on both the availability of precursors and the oxidative capacity of the atmosphere. This data analysis task is aimed at bettering our understanding of the reactive nitrogen partitioning observed during the California Regional PM_{10} and $PM_{2.5}$ Air Quality Study (CRPAQS) measurement phase and relating variations in that partitioning to the coincident oxidative conditions. One of the first steps in this analysis is to assess the reliability of the various NO_y components (nitric oxide (NO), nitrogen dioxide (NO_2), peroxy acetyl nitrate (PAN), nitric acid (HNO_3), and particulate nitrate, (collectively $NO_{y(i)}$) that were measured. It is understood that PAN data will be available for a limited number of episodes and that HNO_3 data are not available from the Angiola core site. In addition, the NO_2 data that is available is limited in temporal coverage.

The objectives of this work were to address the following questions for the reactive nitrogen species:

1. What is the comparability and equivalence among collocated sampling methods, what are the biases of one instrument with respect to others, and how should these biases be minimized?
2. What is the quality of the NO_y and $NO_{y(i)}$ species data collected? If some bias in the data is found, what utility might the data still have (e.g., establishing limits on the concentration of some species)?
3. How do the established data quality bounds limit the utility of the reactive nitrogen data to illustrate the chemical and physical processes that link the primarily gas-phase reservoir of reactive nitrogen to particulate matter (PM) concentration issues?

2. TECHNICAL APPROACH

Continuous measurements of NO_y and a number of nitrogen species components were made at the anchor sites during the CRPAQS winter measurement period. We evaluated these measurements and characterized the partitioning among these species by making various comparisons as a function of site, time of day, and other chemical and physical characteristics. This data analysis task is aimed at evaluating and documenting the quality of the reactive nitrogen species measurements and improving our understanding of the reactive nitrogen partitioning observed during the CRPAQS measurement phase and relating variations in that partitioning to the coincident oxidative conditions. The results of this task will serve to establish qualitative confidence limits on the evaluation of processes leading to the formation of particulate nitrate from its precursor species.

Data Availability

Continuous air quality data was collected for a number of reactive nitrogen species at the anchor sites during the winter measurement periods, typically mid-November 2000 through mid-February 2001 (see **Table 2-1**). These measurements include NO_y and its major components NO, NO_2, PAN, nitric acid, and aerosol nitrate. All these measurements were made at a time resolution of 5 or 10 minutes (see **Table 2-2**). Tables 2-1 and 2-2 also show the data availability and time resolution of several additional parameters that might influence the nitrogen species partitioning including ozone, $PM_{2.5}$ and PM_{10} mass, and light scattering. Evaluation of the reactive nitrogen budget required integration of the NO, NO_2, PAN, HNO_3, and NO_y measurements over the sample period of the nitrate measurement.

Table 2-1. Continuous nitrogen species measurements used in this analysis (and selected other continuous measurements) made at the Angiola, Bakersfield, Fresno, Bethel Island, and Sierra Nevada Foothills sites.

ID	Site Instrument	Angiola	Bakersfield	Fresno First Street	Bethel Island	Sierra Nevada Foothills
A	Nephelometer	2/1/00–2/16/01	1/27/00–4/18/01	12/1/99–2/1/01	11/15/00–2/15/01	11/2/00–2/8/01
G	Aethalometer	1/12/00–3/29/01	1/20/00–2/19/01	12/1/99–2/1/01	11/17/00–2/15/01	11/19/00–2/14/01
J	PM_{10} BAM[a]	1/21/00–3/29/01	1/21/00–4/9/01	12/1/99–2/1/01	-	11/19/00–2/12/01
K	$PM_{2.5}$ BAM[a]	1/21/00–3/29/01	1/21/00–4/18/01	12/1/99–2/1/01	11/17/00–2/15/01	11/19/00–2/12/01
N	PAN/NO_2	11/19/00–2/12/01	10/11/00–2/12/01	12/10/00–2/1/01	11/22/00–2/12/01	11/10/00–2/13/01
O	NO_y	12/20/99–2/23/01	12/16/99–3/26/01	12/1/99–2/1/01	11/18/00–2/15/01	11/16/00–2/15/01
P	O_3	1/22/00–2/21/01	Ongoing (ARB)[c]	Ongoing (ARB)[c]	Ongoing (BAAQMD)[b]	11/3/00–2/13/01
Q	Nitrate	11/19/00–3/2/01	11/15/00–3/6/01	11/13/00–2/101	11/28/00–2/6/01	11/20/00–2/12/01
R	HNO_3	11/21/00–2/26/01	–	11/30/00–2/1/01	–	11/16/00–2/15/01

[a] Beta Attenuation Monitor
[b] Bay Area Air Quality Management District
[c] California Air Resources Board

Table 2-2. Time resolution of continuous nitrogen species measurements (and selected other continuous measurements) made at the Angiola, Bakersfield, Fresno, Bethel Island, and Sierra Nevada Foothills sites.

ID	Instrument	Time Resolution (minutes)
A	Nephelometer	5, 60
G	Aethalometer	5, 60
J	PM_{10} BAM	60
K	$PM_{2.5}$ BAM	60
N	PAN/NO_2	5, 60
O	NO_y	5, 60
P	O_3	5, 60
Q	Nitrate	10, 60
R	HNO_3	5, 60

The primary focus of this analysis was to make an assessment of the reliability of the NO_y measurements. For example, we compared the NO_y measured by the NO/NO_y monitor with the NO_y measured by the nitric acid monitor. Consistency between these two NO_y measurements will promote confidence in the nitric acid measurements. We conducted NO_y comparisons for each site and for various times during the CRPAQS winter measurement periods to evaluate the comparability of the two NO_y measurements. Any bias discovered between the collocated measurements of NO_y will help to establish uncertainty bounds for subsequent evaluation of the reactive nitrogen budget.

Next, the other NO_y species measured (PAN, HNO_3, particulate nitrate) were examined primarily in relationship to their contribution to NO_y. This examination of the reactive nitrogen reservoir can be helpful in describing the dynamic and chemical history of an air mass (Buhr et al., 1990; Trainer et al., 1991). Finally, the ratio $\Sigma NO_{y(i)}/NO_y$ will be examined to determine the overall consistency of the reactive nitrogen species data set.

Further analysis incorporated other chemical and physical parameters as needed to generate a better understanding of the conditions that lead to formation particulate nitrate.

3. RESULTS AND DISCUSSION

The measurements collected during the CRPAQS experiment that lend themselves to a detailed examination of reactive nitrogen partitioning are limited to the winter intensive portion of the operations, nominally December 1, 2000 through February 15, 2001. Those measurements included NO_y (total reactive nitrogen measured with a heated molybdenum converter), NO, NO_2 (measured using a gas chromatograph and luminol chemiluminescence detector), PAN (also measured with the luminol detector-based gas chromatograph), particulate nitrate (measured both with a continuous method and via filter-based discrete sampling), and HNO_3 (measured using the discrete filter samples). While the winter period was clearly the most important to understand from the perspective of particulate nitrate formation, it is useful to understand the differences observed between the seasons to better understand the driving forces behind reactive nitrogen oxidation.

Figure 3-1 shows the diurnal variation of the NO/NO_y ratio observed at the Angiola field site during each of the CRPAQS intensives. Among the notable features of this plot is the progression toward higher morning maxima going from summer through fall to winter, and the lower afternoon/evening ratio in the summertime measurements. While it is possible that there is a seasonal difference in the valley-wide source strength of NO emissions, most of the differences observed can be attributed to a combination of greater vertical mixing, and thus greater dilution, during the summer months; and greater photochemical activity leading to the conversion of NO to more oxidized NO_y species.

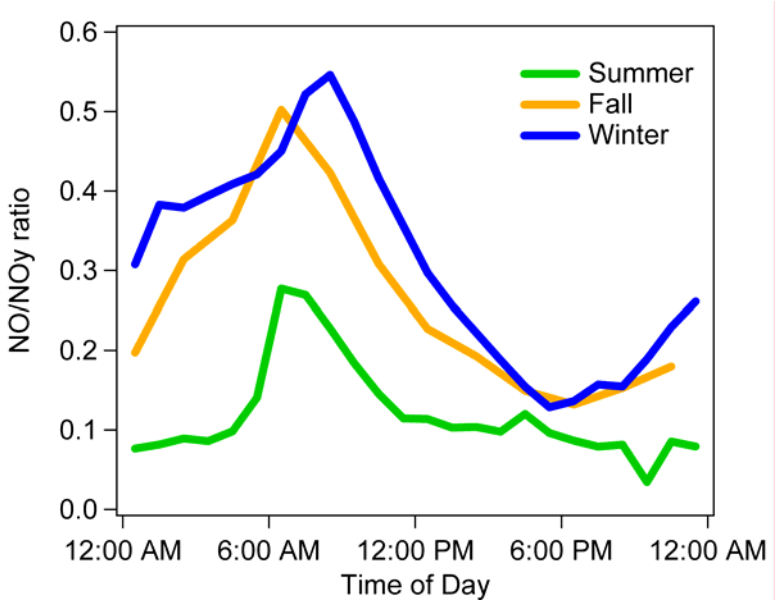

Figure 3-1. NO contribution to NO_y measured at the Angiola site during different seasons.

The same factors, dynamics and chemistry, affect the shape of the fall and winter diurnal profiles. Examination of the other reactive nitrogen species contribution to NO_y during the

winter intensive can serve as a starting point for separating these effects and thereby lead to a greater understanding of the processes that lead to nitrate particle formation. The analysis presented here focuses on understanding the quality of the reactive nitrogen data collected through examination of the correlation of collocated samplers, the absolute and diurnal behavior of the individual species contributions to NO_y, and through a qualitative examination of the dependence of that contribution on other chemical and physical factors.

3.1 DATA INCLUDED IN THE ANALYSIS

The data included in the analysis were the NO, NO_2, PAN, nitrate, HNO_3, and NO_y measurements available in the Central California Air Quality Studies (CCAQS) database in the early spring of 2004 from the Sierra Nevada Foothills (SNF), Bethel Island (BTI), Fresno First Street (FSF), Bakersfield (BAC), and Angiola (ANG) anchor sites. For the purposes of this evaluation the data were integrated over the slowest time base, in this case the filter nitrate measurements. For most of the field sites this resulted in approximately 75 integrated samples. There were some differences in the methods used for the various species measurements at the different sites so it is useful to examine those methods explicitly at the onset of the analysis.

3.1.1 NO Data

The NO data collected at all of the sites was performed using $NO+O_3$ chemiluminescence instruments.

3.1.2 NO_2 Data

The NO_2 data collected at the ANG, BAC, SNF, and BTI sites was performed using a combination gas chromatograph/luminol chemiluminescence instrument. The NO_2 measurement performed at the FSF site was based on the difference in signal between the internal catalytic converter of a $NO+O_3$ chemiluminescence instrument.

3.1.3 PAN Data

The PAN data collected at the ANG, BAC, SNF, and BTI sites was performed using the same combination gas chromatograph/luminol chemiluminescence instrument used for the NO_2 measurements at those sites. There were no PAN measurements collected at the FSF site.

3.1.4 Nitrate Data

Particulate nitrate measurements were performed using two different systems at each of sites. First, discrete filter samples were collected at each of the sites over the course of two to six hours for a total of five samples per day during the intensive operation periods (IOPs) of the winter intensive. In addition, at each of the sites there were continuous nitrate analyzers based on flash vaporization of particle samples impinged on a metal strip, followed by analysis using

an $NO+O_3$ chemiluminescence instrument. The data from the continuous instrument at the FSF site was not available at the time this analysis was performed.

3.1.5 NO_y Data

NO_y data was collected at each of the sites using an inlet-mounted, heated molybdenum catalytic converter followed by an $NO+O_3$ chemiluminescence instrument. In theory, the catalytic converter should convert all of the individual NO_y species to NO. In practice, the NO_y instrument at FSF was operated with an inlet filter, so that particular NO_y measurement should represent NO_y less the portion of the particulate nitrate trapped on the inlet filter.

3.1.6 Ancillary Physical and Chemical Data

Additional measurements collected at each of the sites that were used in this analysis include ozone, light scattering, temperature, and relative humidity. However, not all of these ancillary parameters were available for all of the IOPs included in the analysis.

3.2 COMPARISON OF COLLOCATED MEASUREMENTS

The first order evaluation of the reactive nitrogen measurements was comparison of the collocated measurement results. These include NO_y at the ANG, SNF, and FSF sites; NO at the FSF site; and continuous versus filter nitrate at all of the sites except for FSF.

3.2.1 NO_y

Comparison of the collocated NO_y measurements is particularly important since most of the analysis presented here is predicated on the understanding that we have an accurate measurement of NO_y. That said, in each case the NO_y comparisons are made using essentially identical systems and any systematic or functional design error could influence both systems. The results of the comparison for the collocated systems at SNF, ANG, and FSF are shown in **Figures 3-2 through 3-4**. The comparisons from both SNF and ANG show excellent agreement (<10% difference from unity). At the least, this suggests that the measurement systems were operated in a consistent fashion, and, at most, suggests that the NO_y measurement systems actually measure NO_y. The comparison observed at the FSF site is markedly worse, but for understandable reasons. It is critical to note that the data represented by value_NOyNOy in Figure 4 were from the standard NO_x instrument that used an internal, rather than inlet-mounted catalytic NO_y converter. It is expected that this difference contributes significantly to the poor correlation seen between the two measurement systems.

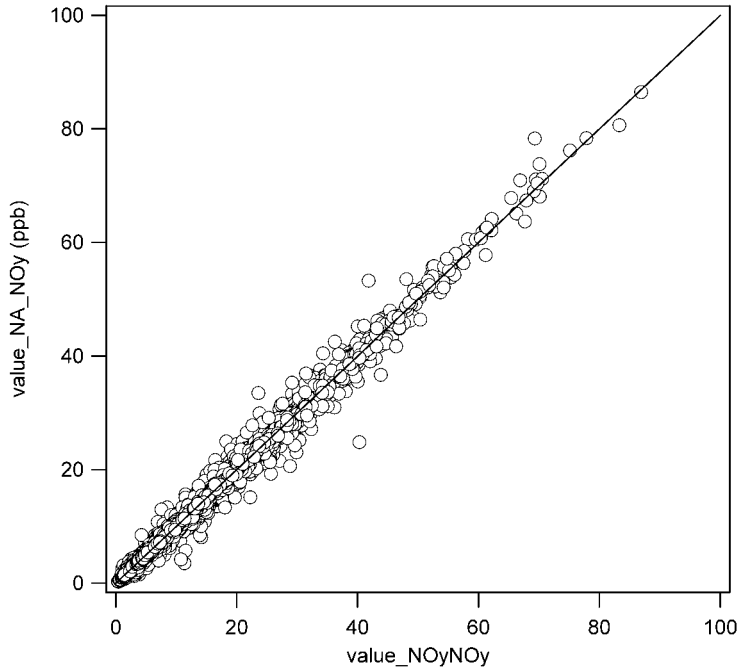

Figure 3-2. Comparison of the collocated NO_y measurements at the Sierra Nevada Foothills site.

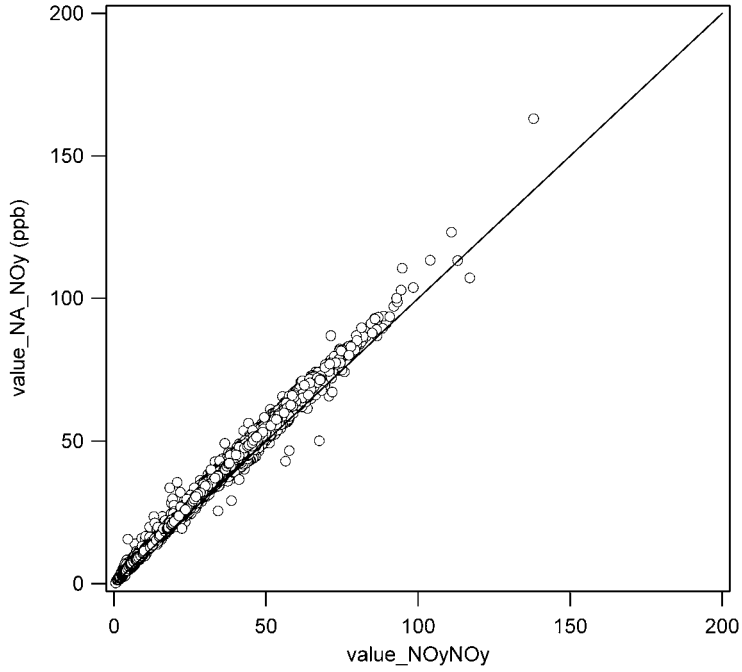

Figure 3-3. Comparison of the collocated NO_y measurements at the Angiola site.

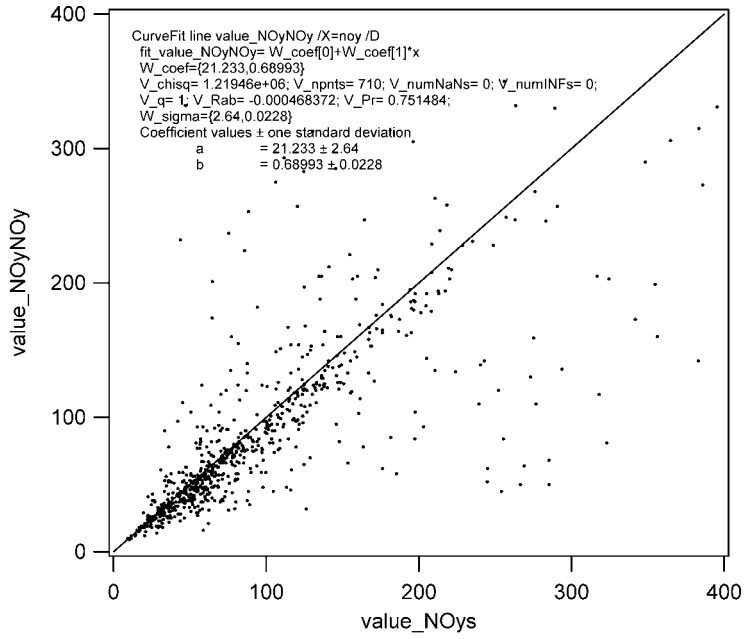

Figure 3-4. Comparison of the collocated NO_y measurements at the Fresno First Street site.

3.2.2 NO

In addition to the different NO_y measurements reported from the FSF site, two different NO measurements were reported as well. These data are shown in **Figure 3-5**. The comparison between the separate NO measurements was considerably better than the separate NO_y measurements from the same instruments. The r^2 for the NO measurements was 0.75 versus r^2=0.56 for the NO_y measurements. While this does not lend much confidence to the NO measurements it is possible that part of the disparity resulted from calibration differences since the standard system was operated by CARB and the custom system was operated by Desert Research Institute (DRI).

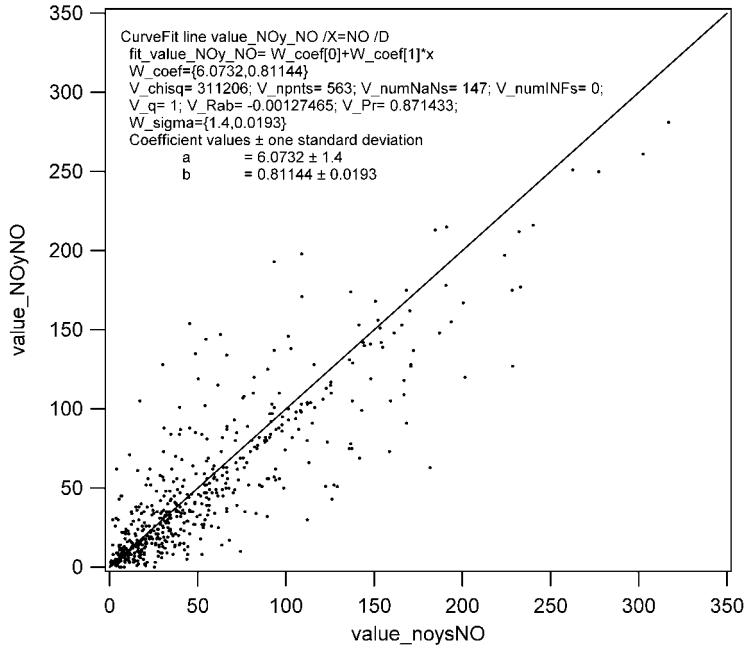

Figure 3-5. Comparison of the collocated NO measurements at the Fresno First Street site.

3.2.3 Nitrate

The comparisons of the collocated nitrate measurements for each of the sites except FSF are shown in **Figures 3-6 through 3-9**. The continuous nitrate measurement was low across the board, relative to the filter-based measurement with the least disparity observed at the BAC site and the greatest disparity observed at the Angiola site. It has been suggested that the continuous nitrate measurements tend towards either under sampling or particle loss (Hering, 2004), which may explain some of the difference observed. It is possible that the sampling loss was less pronounced at the Bakersfield site, resulting in the better correlation between the continuous and filter measurements. The agreement between the two methods is best at low concentrations with deviations at higher levels of 10-50%. For the purposes of understanding the relationship between the sum of the reactive nitrogen species and NO_y, the filter-based measurements were used except for the ANG data where both quantities were calculated.

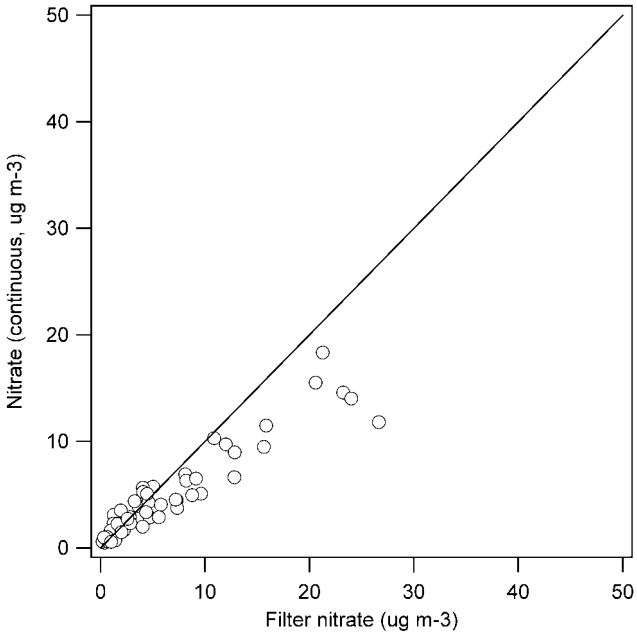

Figure 3-6. Comparison of the collocated nitrate measurements at the Sierra Nevada Foothills site.

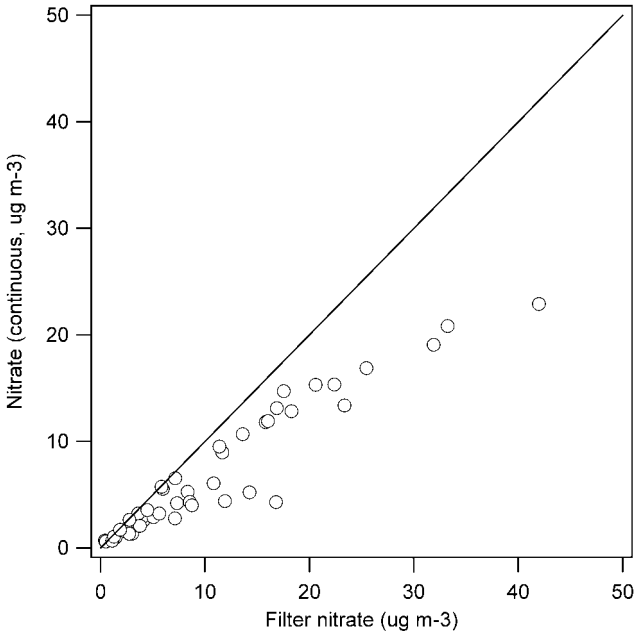

Figure 3-7. Comparison of the collocated nitrate measurements at the Bethel Island site.

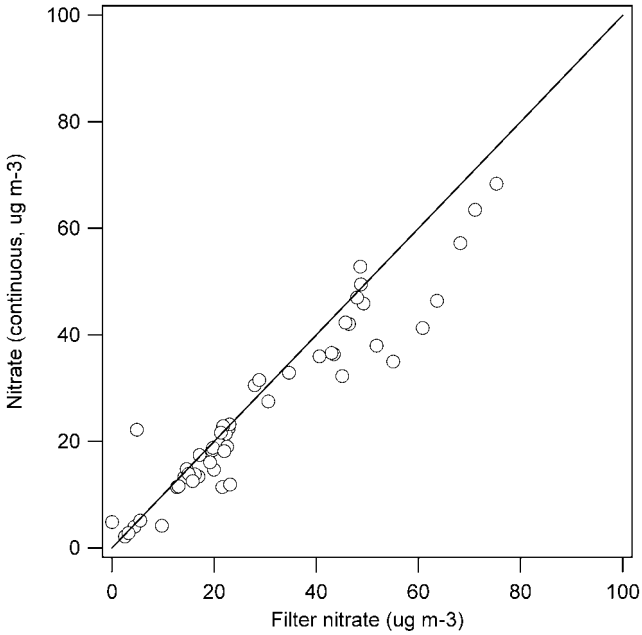

Figure 3-8. Comparison of the collocated nitrate measurements at the Bakersfield site.

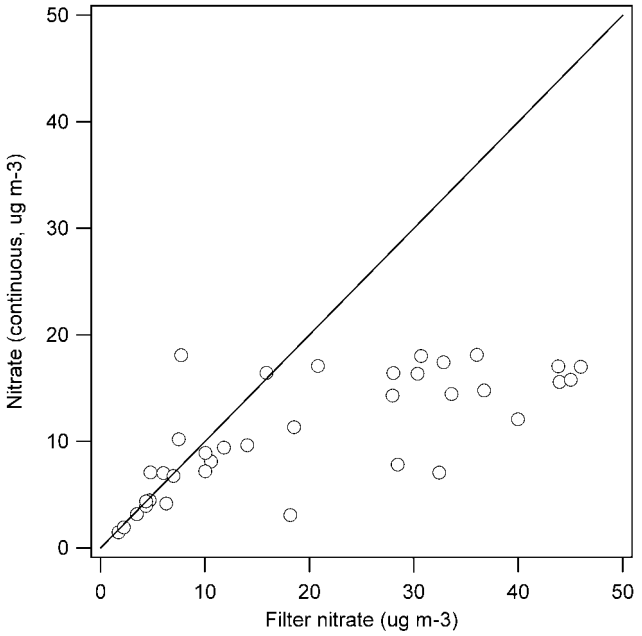

Figure 3-9. Comparison of the collocated nitrate measurements at the Angiola site.

3.3 NO_Y PARTITIONING

3.3.1 Individual Species

A comparison of the individual NO_y species to NO_y is presented for each of the sites in **Figures 3-10 through 3-14**. It is important to note that for the FSF site (Figure 3-11) there are no PAN or continuous nitrate data and the data points indicated for those species are at zero value for that reason. These correlation plots were examined qualitatively from the perspective of correlation of the individual species with NO_y and quantitatively from the perspective of absolute contribution to NO_y. In connection with the latter, NO_2 was observed to exceed NO_y periodically at the SNF and BTI sites. Since this is not physically possible, the observation suggests that either the NO_y measurements at these sites were biased low or, more likely as discussed below, the NO_2 measurements at these sites were biased high.

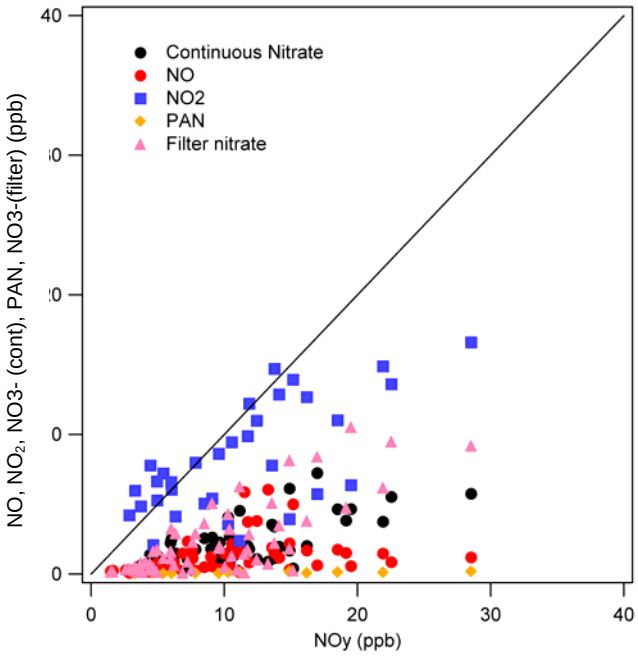

Figure 3-10. Contribution of the individual nitrogen species to NO_y at the Sierra Nevada Foothills site.

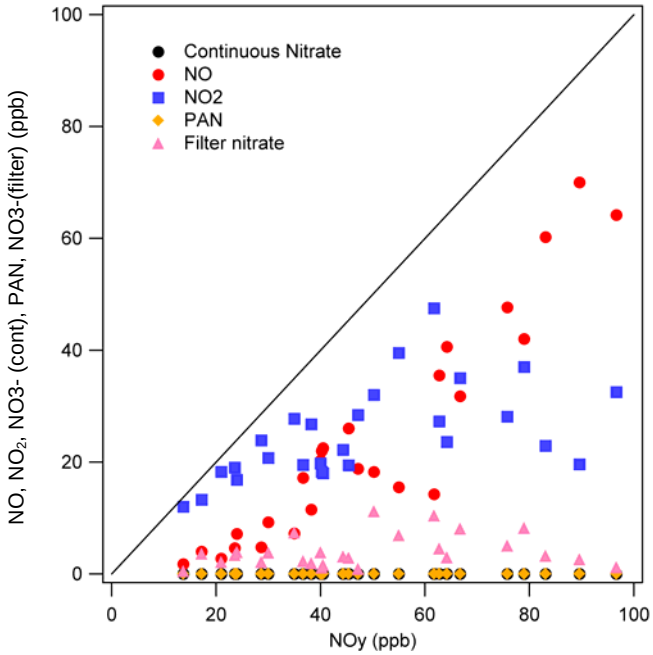

Figure 3-11. Contribution of the individual nitrogen species to NO_y at the Fresno First Street site.

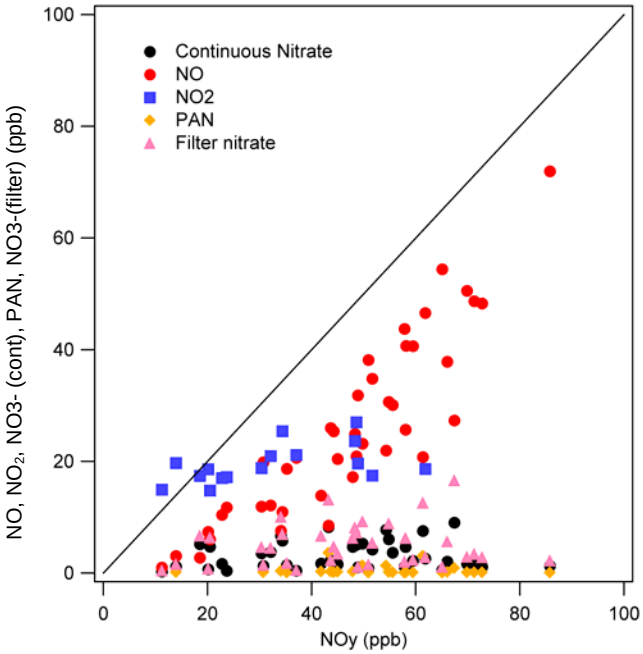

Figure 3-12. Contribution of the individual nitrogen species to NO_y at the Bethel Island site.

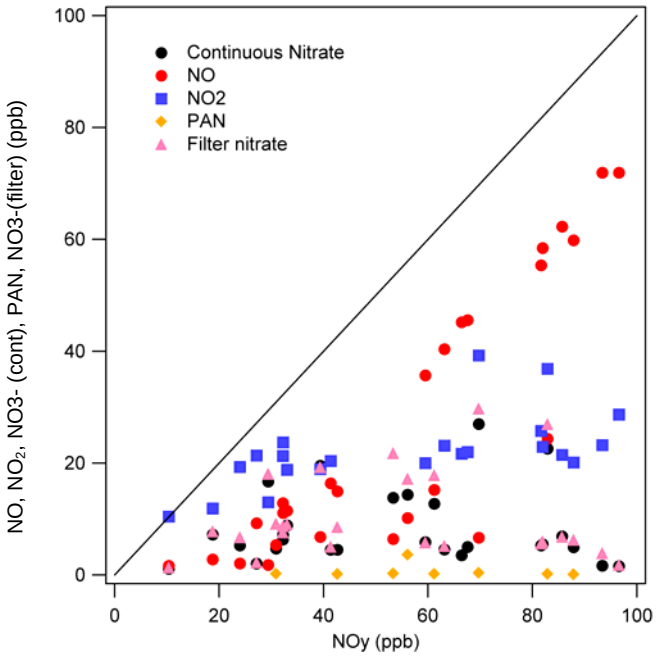

Figure 3-13. Contribution of the individual nitrogen species to NO_y at the Bakersfield site.

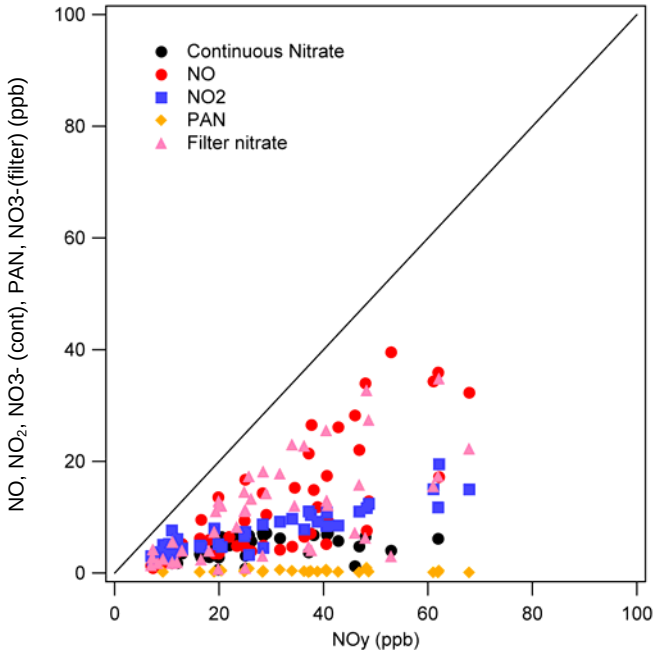

Figure 3-14. Contribution of the individual nitrogen species to NO_y at the Angiola site.

Despite the occasional apparent overestimates of the individual species, there is good correlation between the individual species and NO_y, with the possible exception of the NO_2 measurements collected at the SNF and BTI sites, where only moderate correlation is observed. Examination of these data suggests that the NO_2 measurements at these sites may have an unaccounted-for positive offset. .In the next section it will become more evident that the NO_2 concentration measured at BTI and SNF probably accounts for the NO_y species imbalance observed overall for these sites.

3.3.2 Diurnal Variation

Examination of the average diurnal variation of the $NO_y(i)/NO_y$ ratio provides significant insight into how the individual species contribute to NO_y at a given site. **Figures 3-15 through 3-19** present this data for the sites examined. Included on each plot is the diurnal variation of $\Sigma NOy(i)/NO_y$. For this analysis, the filter-based nitrate measurement, converted to ppbv assuming standard temperature and pressure, was used in calculation of the sum. Comparison of the pattern of $\Sigma NOy(i)$ with that of the individual species is particularly instructive for gaining an understanding of which species may be responsible for any overestimates of NO_y by $\Sigma NOy(i)$.

Figure 3-15 presents the data collected at the SNF site. On average, the $\Sigma NOy(i)$ overestimates the observed NO_y by more than 20%. The individual contributions shown in Figure 3-15 suggest that the NO_2 concentration may be grossly overestimated. This is supported by the observation that NO_2 alone accounts for more than NO_y during many periods and the variation of NO_2/NO_y is quite similar to $\Sigma NOy(i)/NO_y$. The physical impossibility of this indicates that the NO_2 observations collected at SNF should be viewed as gross overestimates. The filter and continuous nitrate measurements at SNF are comparable in contribution to NO_y and show a distinct diurnal trend with a midday maximum. It is likely that the nitrate diurnal profile results from transport processes. Given that the NO_2 measured at the SNF site was overestimated, the true contribution of the other species would be relatively higher.

The data presented in Figure 3-16 for the FSF site shows excellent balance between NO_y and $\Sigma NOy(i)$. In part this is due to the fact that the NO_2 measurement is calculated by the difference between an internal catalytic converter and NO measured with the same instrument. That said, if this measure of NO_2 is in error it will be higher than the true value rather than lower. This contention is supported by the observation that the NO_2 contribution increases during the middle of the day while we expect it to decrease due to photochemical activity. Nonetheless, the $\Sigma NOy(i)$ value is within 10% of unity on average. It is important to note that the measured HNO_3 contribution to NO_y is not included in the sum (HNO_3 was not included to provide consistency with the sites that do not have this measurement). Separate analysis indicates that the HNO_3 contribution is on the order of 4% and does not significantly impact the $\Sigma NOy(i)$ value.

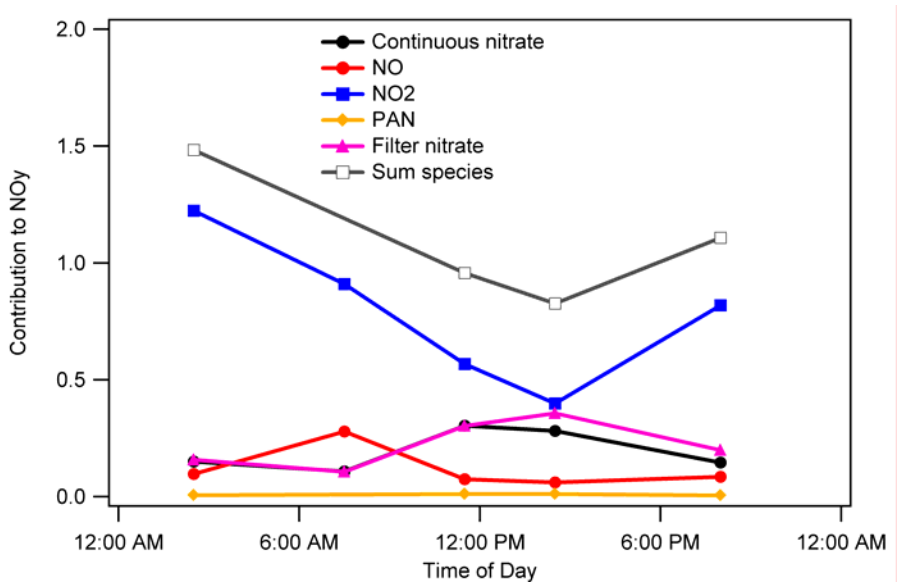

Figure 3-15. Diurnal variation of NO_y partitioning at the Sierra Nevada Foothills site.

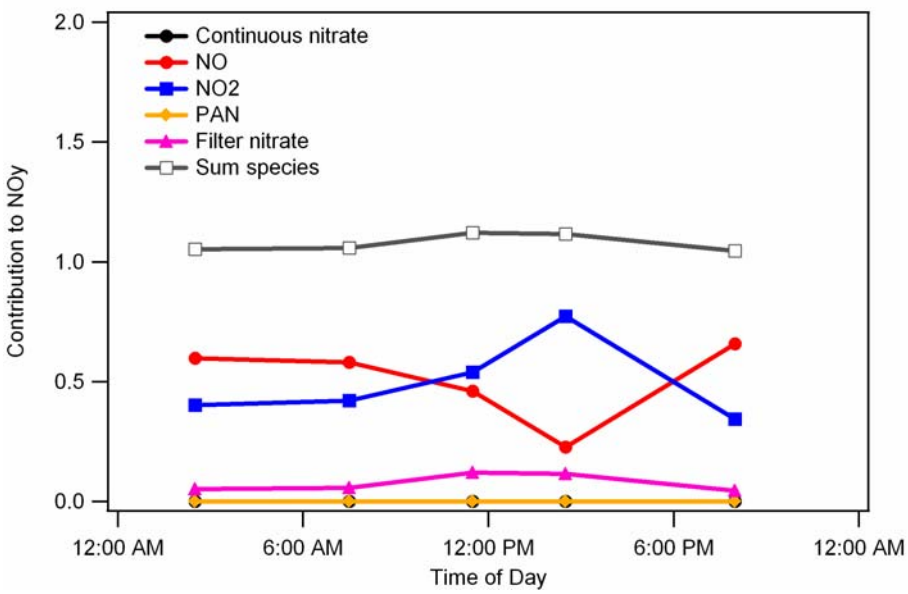

Figure 3-16. Diurnal variation of NO_y partitioning at the Fresno First Street site.

The data shown in Figure 3-17 represent the diurnal NO_y partitioning at the BTI site. The data from BTI are quite similar to those observed at SNF, including both the gross overestimate of ΣNOy(i), overestimated by 30% on average, and the probable contribution of NO_2 to that overestimate.

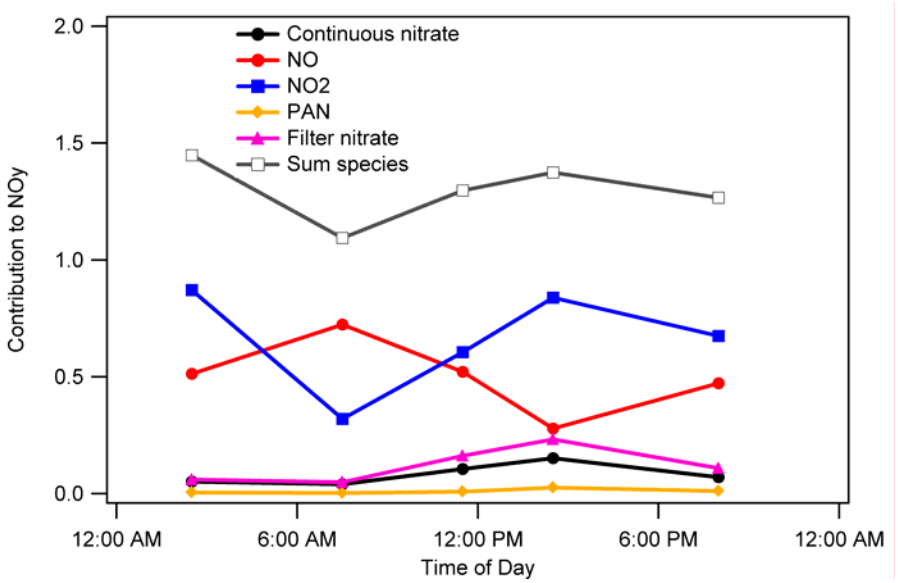

Figure 3-17. Diurnal variation of NO_y partitioning at the Bethel Island site.

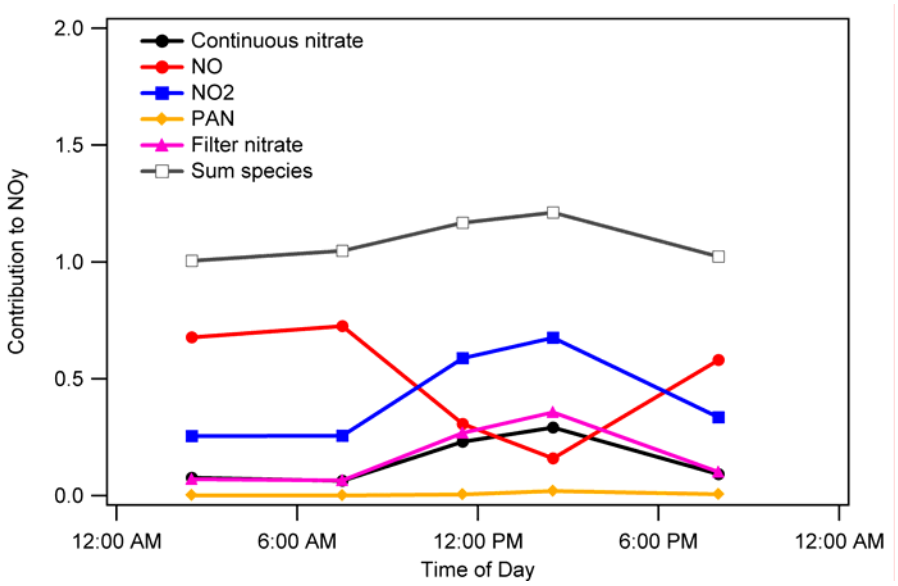

Figure 3-18. Diurnal variation of NO_y partitioning at the Bakersfield site.

The data shown in Figure 3-18 represent the diurnal NO_y partitioning observed at the BAC site. Our expectation is that the contribution to NO_y from nitrate should increase during the day due to photochemical processes while at the same time the contribution from NO_2 should probably decrease during the day for the same reasons. Thus we submit that it is the NO_2 contribution that drives the quantity $\Sigma NOy(i)$ out of balance during the daytime hours. That said, the NO_y balance at BAC is within 10% of unity on average.

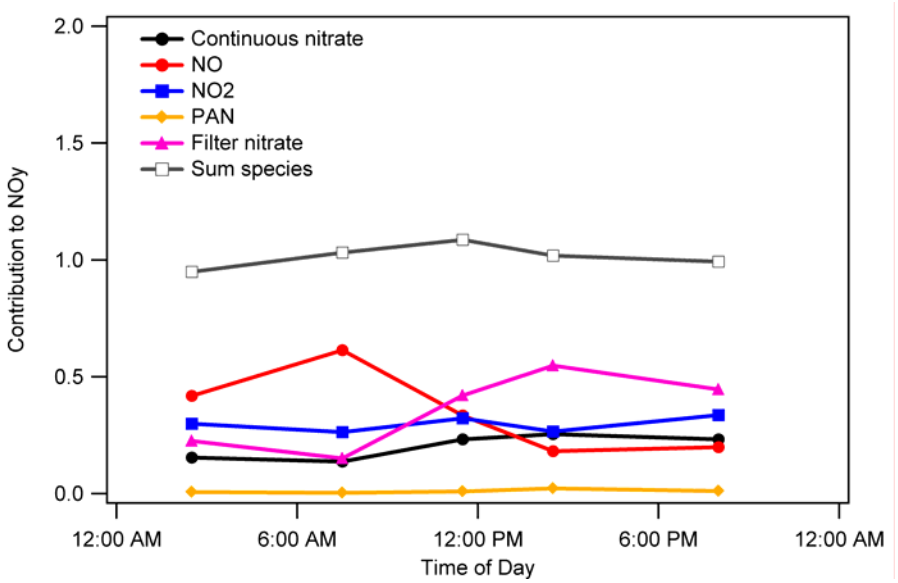

Figure 3-19. Diurnal variation of NO_y partitioning at the Angiola site.

The data shown in Figure 3-19 represent the diurnal NO_y partitioning observed at the ANG site. Different than the other sites, the NO_2 contribution at ANG is relatively low (~30%) and shows the expected decrease during the daytime hours. The unique features at ANG is the large contribution of filter nitrate to the total NO_y budget and the disparity between the filter and continuous nitrate measurements. As was discussed in Section 3.2.3, the filter nitrate is often as much as twice as high as the continuous nitrate. The large contribution of nitrate to NO_y at this site may be due to the longer photochemical processing times associated with this more regional site. This contention is supported by the persistence of the nitrate peak into the last sampling period. The other regional sites, SNF and BTI, would likely show a nitrate contribution similar to ANG if the data from those sites were not skewed by the overestimated NO_2 contribution. The NO_y balance measured at the ANG site was the best observed, being within a few percent unity, on average.

3.4 NO_y PARTITIONING AS A FUNCTION OF OTHER PHYSICAL AND CHEMICAL PARAMETERS

The analysis presented thus far has focused on the internal consistency of the reactive nitrogen measurements. In this section the analysis will be extended to examine the species contribution to NO_y as a function of other chemical and physical parameters including temperature, ozone, and light scattering. On one hand this analysis could be useful in furthering our understanding of particulate nitrate formation. However, in this analysis we will examine the relationships observed in a qualitative sense to better understand the disparities observed in the reactive nitrogen balance. Inclusion of the continuous nitrate measurements in this analysis was performed for both consistency and for the possibility that a better understanding of the probable sampling issues would be elucidated.

3.4.1 Temperature

Figures 3-20 through 3-23 show the relationship between the $NO_y(i)/NO_y$ ratio as a function of ambient temperature for the SNF, FSF, BAC, and ANG sites. In general, the strongest relationship we might expect to see is a negative, though not necessarily linear, relationship between nitrate and temperature. There is not strong evidence for this relationship with the possible exception of the ANG data (Figure 3-23). However, in the same data we also see increasing nitrate with increasing temperature. The BAC nitrate data (Figure 3-22) also show an increase in nitrate with increasing temperature. In both cases the relationship suggests an artifact, possibly due to temperature differentials between the ambient and enclosure environments. One conceivable phenomenon is off-gassing/release of HNO_3 or HNO_3 bearing particles from the sample inlet piping as the piping warms up either in the ambient or enclosure environment. The increase in nitrate with increasing temperature may also be due mixing down of aloft nitrate. Finally, it is notable that most of the sites show a decrease in NO with increasing temperature which may be understood to result form both increased mixing (dilution) and increased photochemistry with the warmer ambient temperature.

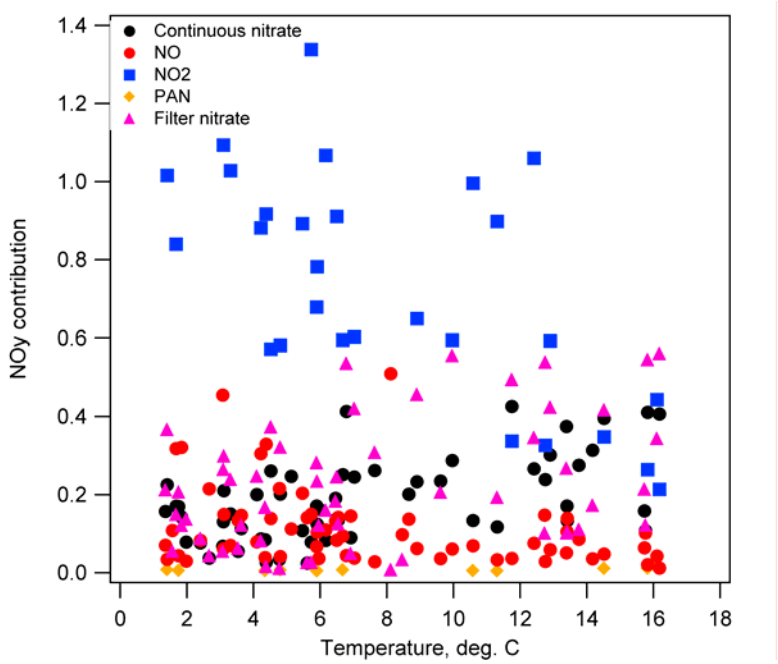

Figure 3-20. Relationship observed between the individual species contribution to NO_y and temperature at the Sierra Nevada Foothills site.

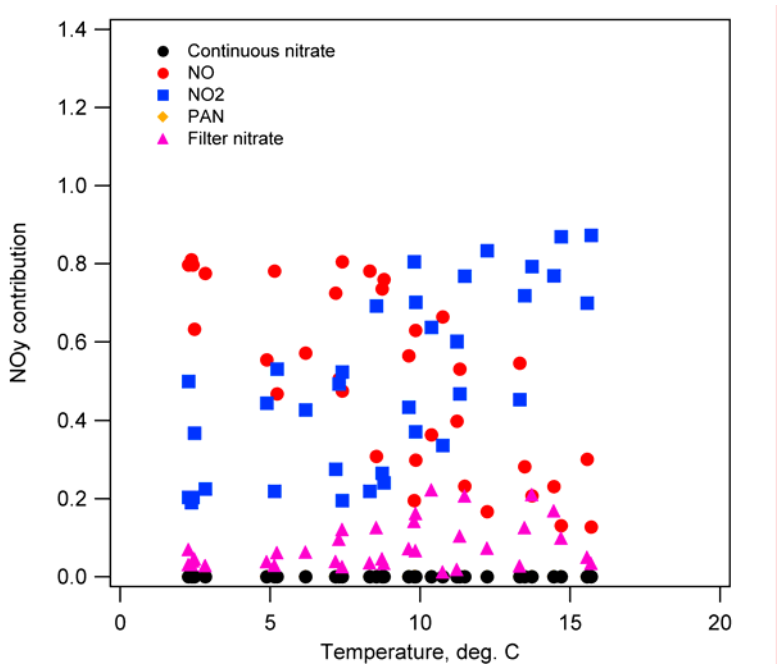

Figure 3-21. Relationship observed between the individual species contribution to NO_y and temperature at the Fresno site.

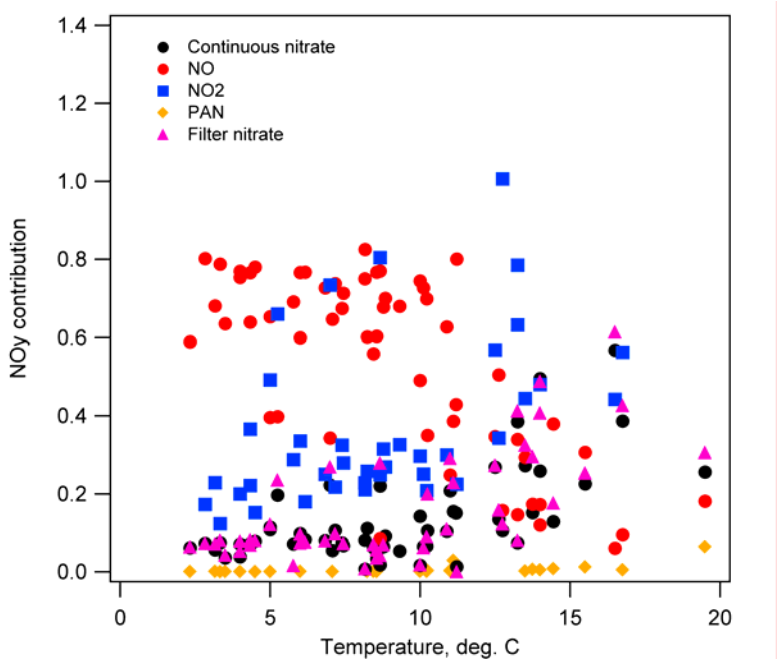

Figure 3-22. Relationship observed between the individual species contribution to NO_y and temperature at the Bakersfield site.

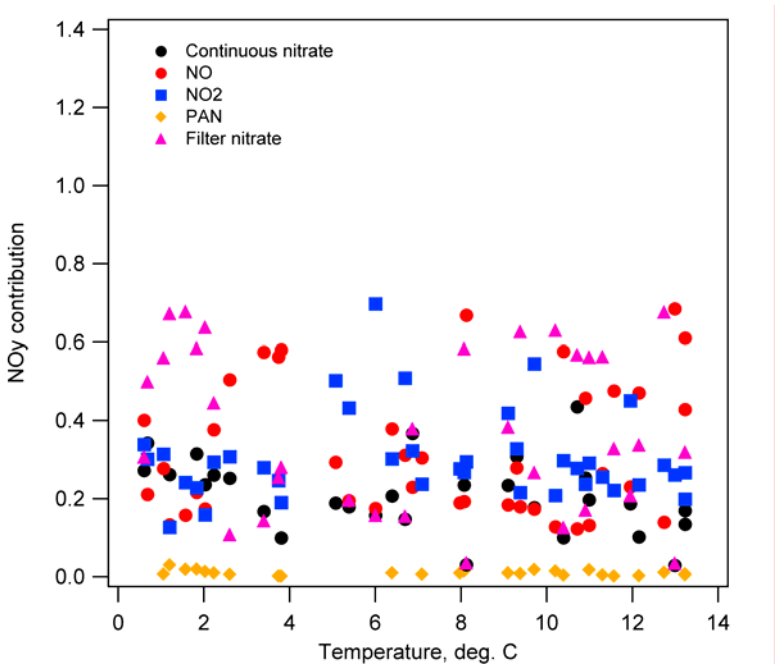

Figure 3-23. Relationship observed between the individual species contribution to NO_y and temperature at the Angiola site.

3.4.2 Ozone

Figures 3-24 through 3-26 show the relationship observed between the NO_y(i) species and ozone observed at the SNF, FSF and ANG sites. Focusing again on the nitrate/NO_y ratio, there may be arguments for either correlation between ozone and nitrate (common photochemical heritage), or anti-correlation (lower temperatures favor nitrate lifetime while tempering ozone formation). In either case, it is remarkable to see both correlation and anti-correlation with ozone from the two separate measures of nitrate collected at the ANG site (Figure 3-26). The continuous nitrate data decrease with increasing ozone while the filter nitrate data show a strong positive relationship. It is not clear what the cause of either relationship is, but the strength of the filter nitrate relationship with ozone suggests that this measurement suffered from an artifact related to some aspect of the chemical or physical framework that supported the photochemical conditions. The data from SNF show a weak positive relationship between nitrate contribution and ozone. The data from the FSF site show an expected relationship between NO, NO_2 and ozone, but little, if any, relationship between nitrate and ozone.

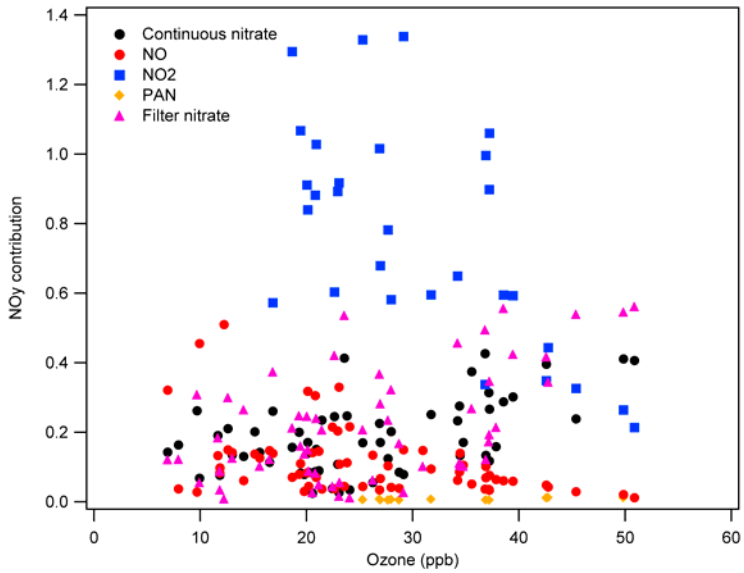

Figure 3-24. Relationship observed between the individual species contribution to NO_y and ozone at the Sierra Nevada Foothills site.

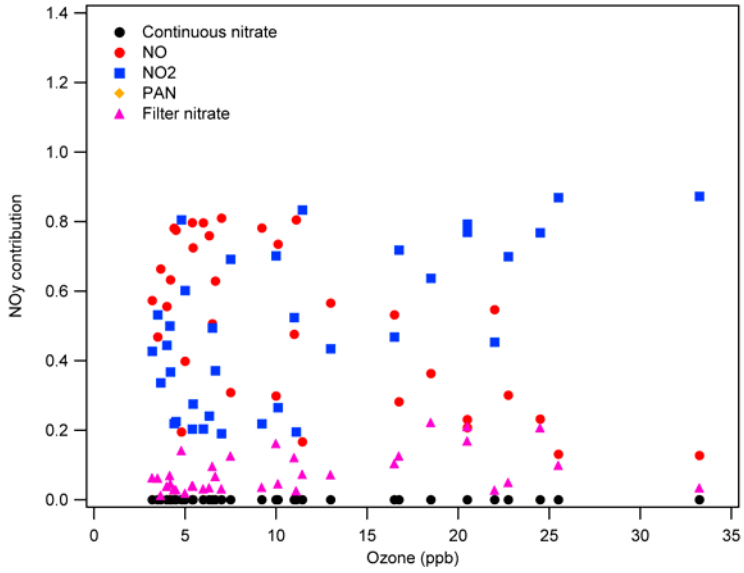

Figure 3-25. Relationship observed between the individual species contribution to NO_y and ozone at the Fresno site.

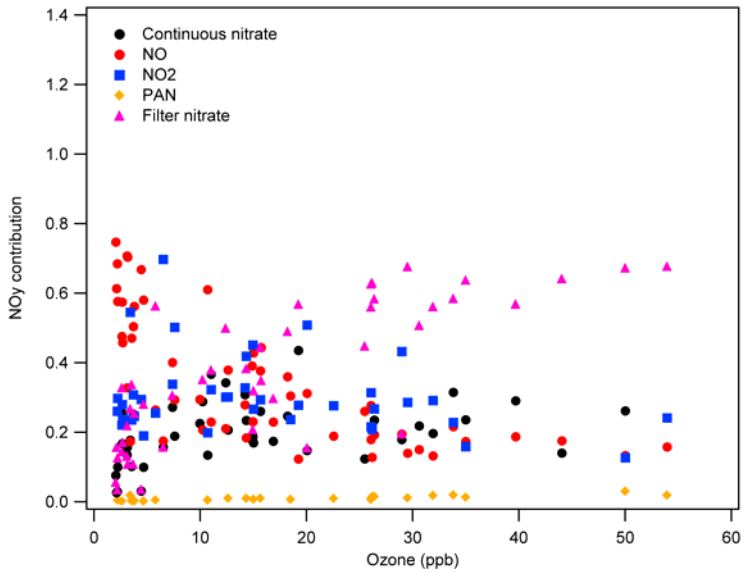

Figure 3-26. Relationship observed between the individual species contribution to NO_y and ozone at the Angiola site.

3.4.3 Light Scattering

Figures 3-27 and 3-28 show the relationship observed between the $NO_y(i)/NO_y$ ratios and light scattering at ANG and BTI. In this case, we might expect to see a positive relationship between nitrate and light scattering. That is the case for the filter nitrate measurements at ANG and both the filter and continuous nitrate measurements at BTI. In contrast, the continuous nitrate measurement at ANG shows a neutral to negative relationship with light scattering. Again, although it is not clear why the two measures of nitrate at ANG demonstrate such different relationships with the ancillary measures, it highlights the fact that the two nitrate measures are not responding to the same thing or one of the measurements is subject to significant artifacts.

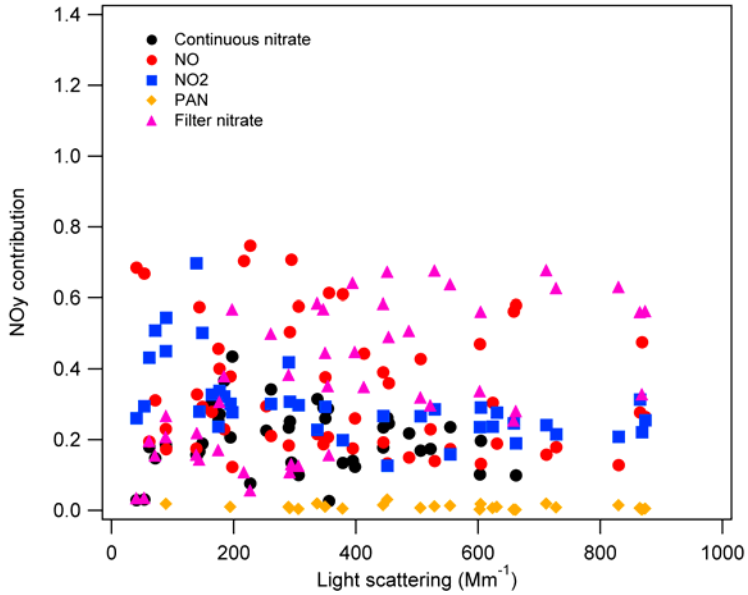

Figure 3-27. Relationship observed between the individual species contribution to NO_y and light scattering at the Angiola site.

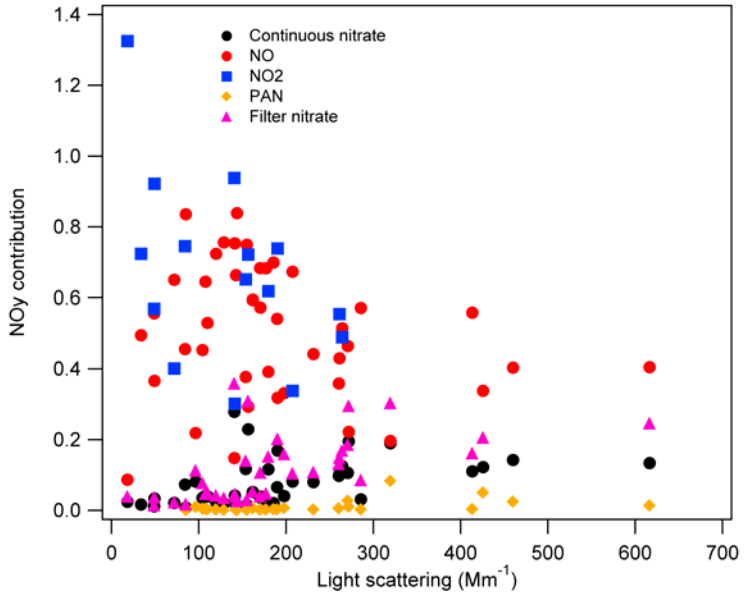

Figure 3-28. Relationship observed between the individual species contribution to NO_y and light scattering at the Bethel Island site.

3.5 DATA QUALITY ASSESSMENTS

Based on the level 2 data validation and analyses presented above, a data quality statement can be made for the different NOy(i) species (see below). In general, these statements

are consistent with the level 1 data validation efforts summarized in the data quality summary reports (see (Hyslop et al., 2003).

3.5.1 NO

The NO measurements collected at each of the sites appear to behave as expected within the reactive nitrogen family and should be used in other analysis without reservation.

3.5.2 NO_2

The NO_2 measurements collected using the GC/luminol system do not seem to represent the expected variability of NO_2 and should not be used in further analysis aimed at understanding chemical processes. The NO_2 measurements reported at the FSF site appear to behave as expected, but are subject to some artifact due to the universal NO_x converter. Those NO_2 measurements might be useful as long as the measurement is understood as an upper limit for the true NO_2 concentration.

3.5.3 PAN

The PAN measurements collected at some of the sites appear to behave as expected within the reactive nitrogen family and should be used in other analysis without reservation.

3.5.4 Nitrate

Nitrate is possibly the most difficult reactive nitrogen species to measure individually. This is supported by the lack of good correlation between the collocated methods. In general terms, the filter-based nitrate data are commonly accepted as the most accurate measure of nitrate. The analysis presented here largely supports that contention and by extension that the filter nitrate data should be used in other analysis without reservation.

3.5.5 NO_y

The NO_y measurements collected at each of the sites appear to behave as expected with respect to the reactive nitrogen family and should be used in other analysis without reservation.

4. SUMMARY

Measurement of the individual components of NO_y and attempts to balance their sum with the NO_y measurement collected during CRPAQS was largely successful. In some cases, most notably the ANG and FSF data, the component parts and total measurement agreed quite well. In other cases the agreement ranged from poor to abysmal. However, the non-uniform NO_y partitioning story present in CRPAQS is not unique—only the most carefully coordinated independent measure of NO_y species result in better understanding the NO_y family. Each site presents a data set that has enormous value, both in the individual species measurements and their relationship to each other. A caution is applicable to the NO_2 measurements at all sites, but particularly where the measurement was made with the luminol-based detector (see Section 3.5.2). In contrast, the results presented here suggest that the measurements of NO, NO_y (where executed with an inlet-based converter), filter nitrate, and PAN can be used with reasonable measurement uncertainty expectations.

5. REFERENCES

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